

First-principles study on stability and magnetism of $\text{NdFe}_{11}M$ and $\text{NdFe}_{11}MN$ for $M=\text{Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn}$

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Recently synthesized NdFe_{12}N has excellent magnetic properties, while it is thermodynamically unstable. Using first-principles method, we study the effect of substitutional 3d transition metal elements to the mother compound NdFe_{12} . We find that Co has positive effect on the stability of the ThMn_{12} structure. In contrast with Ti substitution, Co substitution does not reduce the magnetization significantly. The crystal field parameter $\langle r^2 \rangle A_2^0$ is nearly unchanged by Co substitution, and nitrogenation to $\text{NdFe}_{11}\text{Co}$ greatly enhances $\langle r^2 \rangle A_2^0$. This suggests that Co is a good candidate as a substitutional element for NdFe_{12}N .

I. INTRODUCTION

Recently, NdFe_{12}N has been synthesized¹ following suggestion by a theoretical work². It exhibits larger magnetization and stronger uniaxial magnetocrystalline anisotropy than $\text{Nd}_2\text{Fe}_{14}\text{B}$ at and above the room temperature. NdFe_{12}N is one of ThMn_{12} -type rare-earth transition-metal alloys, where Nd atoms occupy the Th sites and Fe atoms occupy the Mn sites. The crystal structure contains high ratio of transition-metal sites to rare-earth sites. It is favorable for achieving large magnetization, hence iron-based ThMn_{12} -type compounds have been studied as potential candidates for permanent magnet materials.^{3–10} It was reported in the late 80's that $\text{SmFe}_{11}\text{Ti}$ has reasonably large magnetization and magnetocrystalline anisotropy. Although $\text{NdFe}_{11}\text{Ti}$ does not show uniaxial anisotropy, interstitial nitrogenation induces strong uniaxial anisotropy, and also increases the magnetization.^{11,12}

The iron-based ThMn_{12} -type compounds are normally synthesized without nitrogen. Nitrogen is doped afterwards into the interstitial sites of the mother compound to improve magnetic properties, if necessary. In the step synthesizing the mother compound, it has been known that $R\text{Fe}_{12}$ is unstable thermodynamically. For applications to permanent magnets, a bulk sample is necessary. However, the synthesis of $R\text{Fe}_{12}$ has been succeeded only as a film sample.^{1,13,14} A third element is necessary to stabilize the ThMn_{12} -type crystal structure as a bulk sample. Thus far, several elements are known to stabilize the structure. In addition to titanium, V, Cr, Mn, Mo, W, Al, Si serve as stabilizing elements when they substitute the Fe sites.^{15–20} The concentration range for stability depends on the element (summarized in Fig. 1 of Ref. 21).

The substitution reduces the Fe content, hence the magnetization of $R\text{Fe}_{12-x}M_x$ is normally smaller than that of $R\text{Fe}_{12}$. For example, Ti substitution does

reduce the magnetization. In fact, the magnetization is even smaller than naive expectation from the iron concentration.^{2,10} This substantial reduction is explained qualitatively by Friedel's concept of virtual bound state.^{2,22,23} Therefore, a substitutional element that stabilizes the crystal structure without substantial magnetization reduction is required for applications to permanent magnets.

In this paper, we give systematic research to find better substitutional elements in terms of the stability, magnetization, and magnetocrystalline anisotropy in $\text{NdFe}_{11}MN$. Our scheme is as follows: We first study the stability of $\text{NdFe}_{11}M$ where M is a 3d transition-metal element from Ti to Zn. We also estimate overall behavior of magnetic moments. Next we will study their nitrogenated crystal to calculate magnetic moments and crystal field parameter $2A_{20}$ for good candidate(s). We follow experimental synthesis process, i.e., synthesizing the mother compounds $\text{NdFe}_{11}M$ first, then, nitrogenating the mother compounds later. Calculated data will be also useful to compare the properties between our theory and experiments at each step. All of these works are carried out in the first-principles calculations.

II. CALCULATION METHODS

We perform the first-principles calculations by using QMAS (Quantum MAterials Simulator)²⁴ which is based on the density functional theory^{25,26} and the projector augmented-wave method.^{27,28} The exchange-correlation energy functional is given by the PBE formula in the generalized gradient approximation.²⁹ We use the open-core approximation for the Nd-4f, in which Nd-4f is not treated as the valence states (see Ref. 30 and references therein). All the calculations are done in the collinear spin alignment and without the spin-orbit coupling. After the calculation, we approximate the total magnetic

moment by hand by adding the total spin magnetic moment of the valence electrons with magnetic moment of the Nd-4*f* open-core contribution $g_J J = 3.273 \mu_B$, where g_J is the Lande *g*-factor and J is the total angular momentum 9/2 as given by Hund's rules. Note that this approximation does not include either the effects of (A) the orbital magnetic moments of other elements (e.g., Fe, Co) or (B) the hybridization of Nd-4*f* with the other orbitals.

In this study, we consider the magnetocrystalline anisotropy based on the crystal-field theory. Within the lowest order approximation based on this theory, contribution of the Nd-4*f* electrons to the magnetocrystalline anisotropy constant is given by

$$K_1 = -3J(J - \frac{1}{2})\alpha_J \langle r^2 \rangle A_2^0 n_R, \quad (1)$$

where n_R is a concentration of Nd atoms and α_J is the Stevens factor, $-7/1089$ for Nd³⁺. $\langle r^2 \rangle A_2^0$ is the crystal field parameter calculated as,

$$\langle r^l \rangle A_l^m = F_l^m \int_0^{r_c} W_l^m(r) \phi^2(r) dr. \quad (2)$$

F_l^m is a prefactor of the real spherical harmonics Z_l^m . Its explicit expressions can be found in, e.g., Ref. 31. W_l^m is the effective potential at the Nd site expanded by Z_l^m . ϕ is the radial function of the Nd-4*f* orbital, which is obtained in GGA with the self interaction correction. We use a cutoff radius r_c as treated in Ref. 32.

III. RESULTS AND DISCUSSION

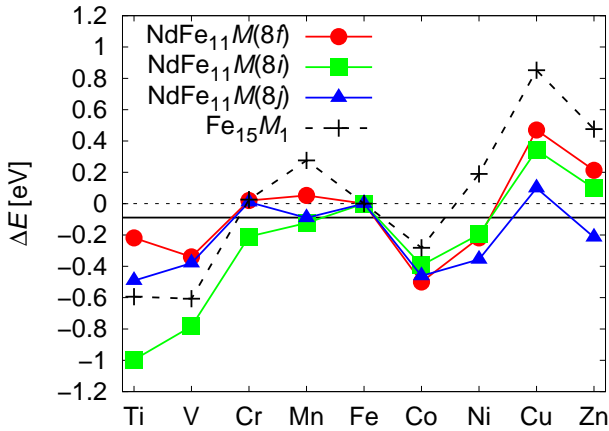


FIG. 1. (Color online) The formation energy of NdFe₁₁*M* defined by Eqs. (3) and (4). The values corresponding to the substitutional sites, 8*f*, 8*i*, and 8*j* are shown as red circles, green squares, and blue triangles, respectively. The formation energy of Fe₁₅*M*₁ calculated with a fixed bcc-Fe lattice is also shown as black crosses. The lines connecting the data points are guides for the eyes.

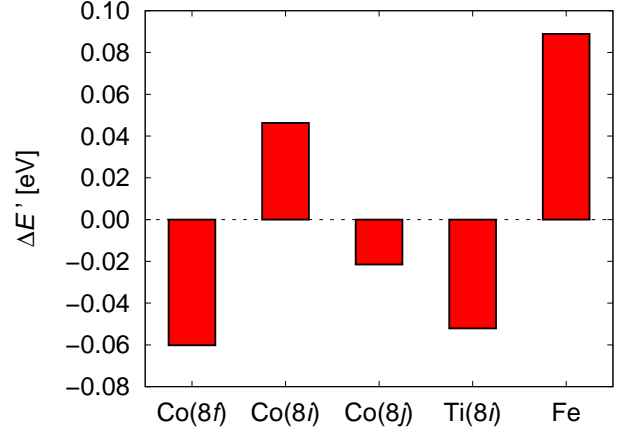


FIG. 2. (Color online) The formation energy of NdFe₁₁Co estimated from the total energy for Nd₂Fe₁₇, bcc-Fe, and CoFe alloy which has CsCl-type crystal structure defined by Eqs. (7) and (8). The results for NdFe₁₁Ti with Ti substituted at 8*i* site and for NdFe₁₂ are shown for comparison.

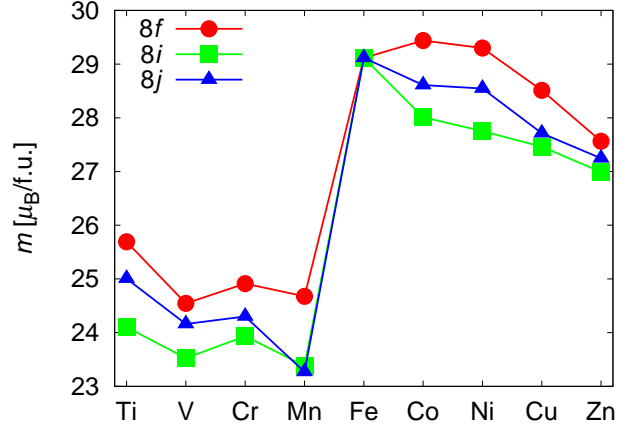


FIG. 3. (Color online) The total magnetic moment m of NdFe₁₁*M* described in μ_B /f.u. The values corresponding to the substitutional sites, 8*f*, 8*i*, and 8*j* are shown as red circles, green squares, and blue triangles, respectively. The lines connecting the data points are guides for the eyes.

First, we discuss stability by substitution in NdFe₁₁*M*. We start from defining a formation energy to measure how much the substitution stabilizes NdFe₁₁*M* compared from NdFe₁₂,

$$\Delta E[M] \equiv E[\text{NdFe}_{11}M] - E_{\text{ref}}[M], \quad (3)$$

$$E_{\text{ref}}[M] \equiv E[\text{NdFe}_{12}] - E[\text{Fe}] + E[M], \quad (4)$$

where $E[\text{NdFe}_{11}M]$, $E[M]$, and $E[\text{Fe}]$ are the total energy of NdFe₁₁*M* per formula unit, the simple substance of *M* per atom, and bcc-Fe per atom with their optimized geometries, respectively.

Figure 1 shows the substitutional element dependence of Eq. (3). The light transition metal elements, Ti, V, Cr, and Mn has negative formation energy. Among them,

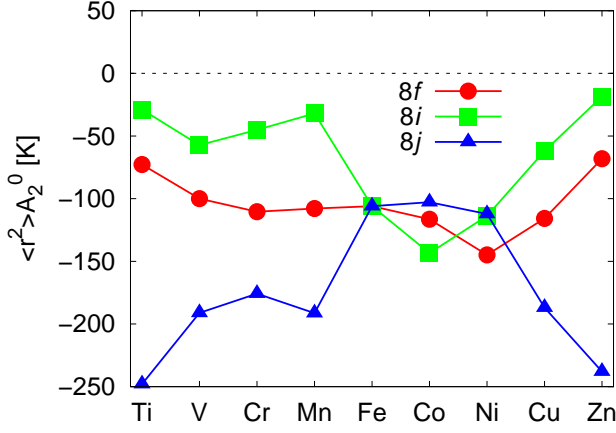


FIG. 4. (Color online) $\langle r^2 \rangle A_2^0$ of $\text{NdFe}_{11}M$ in units of K. The values corresponding to the substitutional sites, $8f$, $8i$, and $8j$ are shown as red circles, green squares, and blue triangles, respectively. The lines connecting the data points are guides for the eyes.

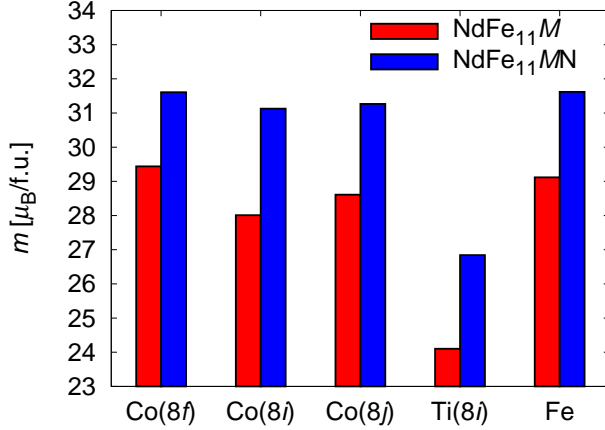


FIG. 5. (Color online) The total magnetic moment m of $\text{NdFe}_{11}\text{Co}$ (red) and $\text{NdFe}_{11}\text{CoN}$ (blue). As a reference, the results for the case of Ti substituted at $8i$ site and for the case without substitution are also shown.

Ti exhibits the largest formation energy in magnitude. The preferable site is the $8i$. The $8j$ site substitution is next preferable, and $8f$ is the most unstable among the three sites. This is consistent with the experimental observation.³³ The order of the preferable sites can be explained by the canonical bond length as discussed in Appendix A. As the atomic number increases, the formation energy for the most preferable $8i$ site substitution becomes less negative. In experiments, the lowest substitution content for phase stability increases in the order of Ti-V-Cr-Mn. This implies that the stabilization becomes weak as the atomic number increases, which is consistent with the order of the calculated formation energy.

As for the right hand side of Fe in the periodic table, Co substitution yields the largest negative formation en-

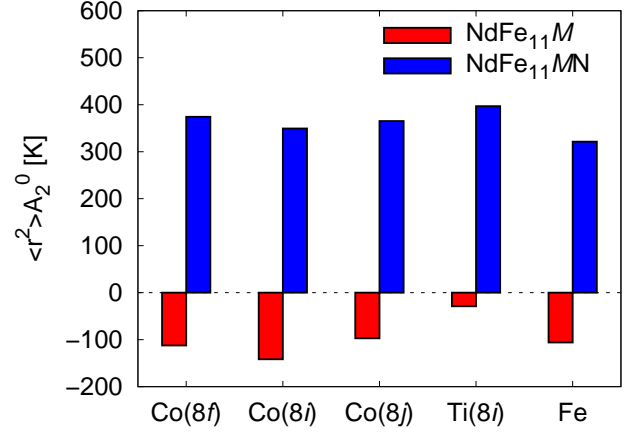


FIG. 6. (Color online) The $\langle r^2 \rangle A_2^0$ of $\text{NdFe}_{11}\text{Co}$ (red) and $\text{NdFe}_{11}\text{CoN}$ (blue). As a reference, the results for the case of Ti substituted at $8i$ site and for the case without substitution are also shown.

ergy. The most stable site for Co is $8f$, and the next favorable site is $8j$. The two sites have similar formation energy. Both $\text{NdFe}_{11}\text{Ni}$ and $\text{NdFe}_{11}\text{Zn}$ also exhibit negative formation energy, but they are less negative than that of Co substitution.

We also plot the calculated formation energy of $\text{Fe}_{15}M_1$ in which M is embedded on the $2 \times 2 \times 2$ bcc-Fe conventional cell,

$$\Delta E[\text{Fe}_{15}M_1] \equiv E[\text{Fe}_{15}M_1] - (15E[\text{Fe}] + E[M]). \quad (5)$$

The lattice for $\text{Fe}_{15}M_1$ is fixed to the optimized bcc-Fe structure. The curve is similar to the formation energy of $\text{NdFe}_{11}M$. $\text{NdFe}_{11}M$ contains a lot of Fe and M dependence of the formation energy can be roughly determined from the coupling of M -Fe. In experiment, the soluble range of $\text{NdFe}_{12-x}M_x$ depends on the substitutional elements. The experimentally observed range of x for each M may reflect the soluble range for the M -Fe alloys.

The horizontal black solid line in Fig. 1 indicates a formation energy of $\text{Nd}_2\text{Fe}_{17}$ measured from NdFe_{12} as a reference system.

$$\frac{1}{2}\Delta E[\text{Nd}_2\text{Fe}_{17}] \equiv \frac{1}{2}E[\text{Nd}_2\text{Fe}_{17}] + \frac{7}{2}E[\text{Fe}] - E[\text{NdFe}_{12}] \quad (6)$$

The calculated value of Eq. (6) is negative. Namely, NdFe_{12} is unstable compared to $\text{Nd}_2\text{Fe}_{17}$ and bcc-Fe. This is consistent with experimental observation. By shifting the energy origin from the black broken line to the black solid line in Fig. 1, we can read the stability of $\text{NdFe}_{11}M$ compared from $\text{Nd}_2\text{Fe}_{17}$.

For $M=\text{Ti}$, V , and Co , the formation energy defined by Eqs. (3) and (4) are large negative values. Among these elements, Ti and V substantially reduce the magnetic moment, while Co does not (later we will describe in detail). In terms of both the formation energy and the magnetic moment, Co is a good candidate as the substitutional element.

The formation energy defined in Eqs. (3) and (4) does not take into account alloying effects. Here, we discuss the alloying effect of Co-Fe for the case of $M=\text{Co}$. We redefine the formation energy of $\text{NdFe}_{11}M$ comparing from $\text{Nd}_2\text{Fe}_{17}$ and a M -Fe alloy.

$$\begin{aligned}\Delta E'[M] &\equiv E[\text{NdFe}_{11}M] - E'_{\text{ref}}[M] \\ E'_{\text{ref}}[M] &\equiv \frac{1}{2}E[\text{Nd}_2\text{Fe}_{17}] + E[M\text{Fe}_x] + \left(\frac{5}{2} - x\right)E[\text{Fe}]\end{aligned}\quad (7)$$

$E[M\text{Fe}_x]$ is the total energy of $M\text{Fe}_x$. Figure 2 shows the calculated formation energy defined by Eqs. (7) and (8). We consider CoFe with the CsCl structure as the reference alloy. For comparison, the results for $\text{NdFe}_{11}\text{Ti}$ (substituted at $8i$ site) and NdFe_{12} are also presented. For $M=\text{Ti}$, TiFe_2 with MgZn_2 structure is calculated as the reference. The calculated formation energy reproduces the experimental observation that synthesis of NdFe_{12} is difficult, while that of $\text{NdFe}_{11}\text{Ti}$ is easy. $\text{NdFe}_{11}\text{Co}$ for $8f$ site substitution has negative formation energy which is as low as that of Ti substitution. Even we still neglect the alloying effect of M in $\text{Nd}_2\text{Fe}_{17}$ in Eq. (8), Co can stabilize the crystal structure.

The substitution affects not only the stability, but also the magnetism of $\text{NdFe}_{11}M$. Figure 3 shows M dependence of the magnetic moments. $\text{NdFe}_{11}M$ with $M=\text{Ti}$, V, Cr, and Mn have much smaller magnetic moments compared to NdFe_{12} . There is a jump in the total magnetic moment between the light transition metals Ti-Mn and the heavy transition metals Fe-Zn. The jump is the result that the magnetic coupling between M and the host Fe is antiferromagnetic for these light transition metals and becomes ferromagnetic for these heavy transition metals (for Cu and Zn, it is marginal, i.e., their local moments are almost zero).

The change of the magnetic moments from $M=\text{Ti}$ to Mn is qualitatively explained in terms of Friedel's concept of virtual bound state²² by noticing that the majority spin d band of NdFe_{12} is nearly filled like in fcc-Ni. By substituting $M(=\text{Ti-Mn})$, the impurity level for the majority spin states appears above the top of the host Fe d band and the Fermi level. The change of the number of the majority spin electrons Δn^\uparrow is -5 . For the minority spin states, the host Fe d band and the impurity level are fairly close and these states can hybridize. The electrons introduced by the substitutional element occupy these hybridized states. The change of the number of the minority spin electrons Δn^\downarrow is $Z(M) - Z_{\text{Fe}} - \Delta n^\uparrow$, where Z_{Fe} is the number of the valence electrons of Fe ($=8$), and $Z(M)$ is those of M , i.e., 4 (Ti), 5 (V), 6 (Cr), 7 (Mn). Then the change in the magnetic moment is given by $\Delta n^\uparrow - \Delta n^\downarrow = -(Z(M) + 2.0) \mu_B$. The deviation from idealistic Friedel's concept is due not only to the fact that the majority spin d band of NdFe_{12} is not completely filled but also to the presence of continuous sp band overlapping the d band. For Mn, the split-off Mn d states are rather close to the Fermi level and the significant portion of their tails are occupied to reduce the magnetic moment reduction.

Co substitution at the preferable site (the tight $8f$ site) works positively to the magnetic moment. For more spacious $8i$ and $8j$ sites, on the other hand, the magnetic moment is slightly smaller than that of NdFe_{12} . This is in contrast with naive expectation from the Slater-Pauling curve that the magnetic moment is increased by slight amount of Co doping to bcc-Fe. In Co doped bcc-Fe, the electronic structure at the Fe sites next to Co is modified due to the upward shift of the minority spin d level of Fe caused by the hybridization with the neighboring Co. The minority spin occupation decreases due to this level shift and the majority spin occupation increases due to the reduction in the Coulomb repulsion from the minority spin electrons. Therefore, the magnetic moment of Fe next to Co increases slightly. The small increase of the magnetic moment at 8 Fe sites over-cancels the reduction of the magnetic moment at Co site. In the present NdFe_{12} case, we see similar behavior at the tight $8f$ site. However, for more spacious sites ($8i$ and $8j$), as the hybridization between Fe d states and Co d states will become weaker, the magnetic moment enhancement at the neighboring Fe sites will be reduced. Another possible reason for the difficulty of magnetic moment enhancement due to Co substitution in NdFe_{12} case may be its smaller bandwidth and consequent nearly filled majority spin d band.³² As the atomic number increases further from Co to Zn, the magnetic moment decreases monotonically.

Next we discuss the effect of substitution on the crystal field parameter $\langle r^2 \rangle A_2^0$. The substitutional element dependence of $\langle r^2 \rangle A_2^0$ is shown in Fig. 4. For $M=\text{Co}$, $8f$ site substitution gives only slightly smaller and $8j$ site substitution exhibits almost the same $\langle r^2 \rangle A_2^0$ compared to NdFe_{12} . Co substitution at the $8i$ site decreases $\langle r^2 \rangle A_2^0$ by about 50 K. While Co or Ni substitution brings small change ($< 50\text{K}$) irrespective of the substitutional site, $\langle r^2 \rangle A_2^0$ for other elements depends strongly on the substitutional site, and the value increases in the order of $8j$ - $8f$ - $8i$. This trend is desirable for the light transition metals, since the preferable site is $8i$. On the other hand, the preferable site for Cu and Zn is $8j$, hence substitution with Cu or Zn is expected to be unfavorable in terms of the magnetocrystalline anisotropy.

Finally, we study the effects of nitrogenation for the good candidate, Co. Figure 5 shows the total magnetic moments of $\text{NdFe}_{11}\text{Co}$ (red), and their nitrogenated compounds (blue). The results for Ti substituted at $8i$ site and for the case without substitution are also shown as references. The total magnetic moments of $\text{NdFe}_{11}\text{Co}$ and their nitrogenated compounds have almost the same values as those of NdFe_{12} and its nitrogenated compound, and have much larger values than those of $\text{NdFe}_{11}\text{Ti}(8i)$, which are previously studied in theories and experiments.^{1,2,11,12,32}

Next the values of $\hat{2}A_{20}$ are shown in Fig. 6 for the compounds corresponding to those in Fig. 5. $\text{NdFe}_{11}M$ have negative values, but their nitrogenated compounds show large positive values as expected. The values of

$\text{NdFe}_{11}\text{CoN}$ is slightly larger than that of NdFe_{12}N and are comparable to the values of $\text{NdFe}_{11}\text{TiN}$. These results suggest that Co works positively in $\text{NdFe}_{11}\text{MN}$, therefore possibly yields another good candidate of high performance bulk magnet materials.

IV. CONCLUSION

We have performed first-principles calculations of $\text{NdFe}_{11}M$ where $M=\text{Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn}$, and a few of their nitrogenated compounds. The calculated formation energy of $\text{NdFe}_{11}\text{Co}$ is negative compared to $\text{Nd}_2\text{Fe}_{17}$, bcc-Fe and CoFe in the CsCl structure, suggesting that $\text{NdFe}_{11}\text{Co}$ could be stable in the bulk. Furthermore, its nitrogenated compound, $\text{NdFe}_{11}\text{CoN}$ enhances the magnetic moment, and has almost the same magnetic moment as that of NdFe_{12}N which is unstable in the bulk. The magnetocrystalline anisotropy of $\text{NdFe}_{11}\text{CoN}$ estimated from the crystal field parameter $2A_{20}$ is almost the same compared to NdFe_{12}N and $\text{NdFe}_{11}\text{TiN}$. These data conclude that Co could be a good substitutional element in $\text{NdFe}_{11}\text{MN}$.

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Appendix A: Space of Fe sites in NdFe_{12}

For a complex crystal structure, it is difficult to describe whether an atomic site has large or small space. In this appendix, we propose a length scale to describe effective sparseness reflecting strength of the hybridization. This length scale can be useful to discuss the preferential substitutional sites in $\text{NdFe}_{11}M$. In addition, the local spin moment can be also discussed using this length.

In NdFe_{12} , there are three Fe sites, $8f$, $8i$, and $8j$. We expect that a preferable substitutional site is explained by the space of each site. To define the space of atomic

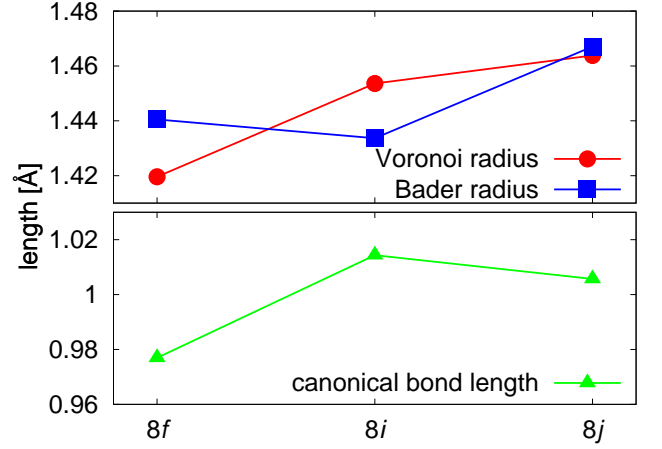


FIG. 7. (Color online) The upper figure shows the lengths estimated from Voronoi cell volume and from Bader cell volume, respectively. The lower figure shows the canonical bond length defined in Eq. (A1). The lines connecting the data points are guides for the eyes.

site, we introduce a length l_μ based on the canonical band theory.³⁴

$$l_\mu \equiv \frac{1}{2} \left(\sum_\nu |\mathbf{r}_\nu - \mathbf{r}_\mu|^{-10} \right)^{-\frac{1}{10}} \quad (\text{A1})$$

where μ specifies the atomic sites, $8f$, $8i$, and $8j$. The summation is taken over the neighboring atoms. The canonical bond length l_μ defined above is a measure of the d - d bond. From the canonical band theory, the d - d hopping integral is proportional to inverse 5th power of the distance between the d orbitals. The bond strength is measured in terms of the width of the d band which is given by a square root of the sum of hopping integral squared (inverse 10th power of the distance) over the neighboring sites of a given site.

Figure 7 shows l_μ for Fe-Fe bonds in NdFe_{12} . For comparison, we also plot the Voronoi radius and Bader radius. The Voronoi and Bader radii are determined so that the volume of the spheres defined by these radii are equal to the volumes of the Voronoi cell and Bader cell, respectively. The Voronoi cell of a μ th atom is defined as a region surrounded by the perpendicular bisection planer boundary between the μ th atom and its neighbors (see Ref. 35 for the details of the calculation). The Bader cell is given by the space decomposition according to the Bader population analysis^{36,37} for sum of the partial electronic core density, the pseudo charge density, and the compensation charge density (their notations are following Ref. 28). Light transition metals such as Ti, which has larger atomic radius than Fe, occupies the $8i$ site. Hence, we naively expect that the $8i$ site is the most spacious site among the $8f$, $8i$, and $8j$ sites. The canonical bond length is consistent with this expectation. On the other hand, the Voronoi radius does not take the maximum value for the $8i$ site, and the Bader radius takes the

smallest value at $8i$.

The relative magnitude of the local spin moment can be also understood by using the canonical bond length. The canonical bond length reflects the strength of the hybridization with surrounding atoms, i.e., larger (smaller) l_μ corresponds to weaker (stronger) hybridization. As the hybridization becomes weaker (stronger), the band width becomes narrower (broader). The band width is roughly in inverse proportion to the amplitude of the density of states. Following the Stoner criterion for ferromagnetism, larger density of states at Fermi level is expected to give stronger spin polarization. Eventually, larger l_μ value is expected to yield stronger spin polarization. The local spin moments of Fe at $8f$, $8i$, and $8j$ sites are 1.78, 2.53, and $2.31 \mu_B$, which is consistent with the expectation from l_μ .

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